

OXYDESULFURIZATION OF COAL TREATED WITH METHYL IODIDE --
IMPLICATIONS FOR REMOVAL OF ORGANIC SULFUR

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Introduction

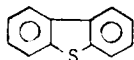
In the chemical desulfurization process being developed at the Ames Laboratory, coal is leached with a dilute solution of sodium carbonate containing dissolved oxygen under pressure and at elevated temperature. For many coals, most of the inorganic sulfur can be removed, and the organic sulfur content can be reduced by 25-40% (1,2). In some instances, as much as 70% of the organic sulfur has been removed. An essential piece of information in evaluating the effectiveness of a process for the removal of organic sulfur is the identity and reactivity of the various sulfur functions grouped under the term "organic sulfur."

Although much data is available on the content and distribution of the so-called pyritic, sulfatic, and organic sulfur in various coals, relatively little has been published on the nature and abundance of the organic sulfur groups in coal. Essentially no data are available on the reactivity of such functional groups under oxidizing conditions, such as those found during oxydesulfurization. In fact, no completely satisfactory method exists as yet for the direct determination of organic sulfur in coal, although a few methods are being developed. These methods are based either on microprobe analysis (3,4), or on low-temperature ashing of the organic components of coal (5), or on their thermokinetic reduction to hydrogen sulfide (6). As a routine, however, organic sulfur is still being determined as the difference between the total sulfur and the amount of the inorganic (i.e., pyritic plus sulfatic) sulfur, according to ASTM procedures.

Attempts to identify and quantitatively determine organic sulfur functions in coal have been few. On the basis of very sparse data, it is generally assumed that the organic sulfur in coal can be described almost completely by the following classes:

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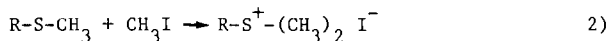
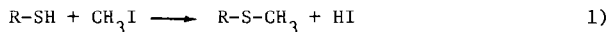
- Class 1. Aliphatic or aromatic thiols (mercaptans, thiophenols): $R-SH$, $Ar-SH$
- Class 2. Aliphatic, aromatic, or mixed sulfides (thioethers): $R-S-R$, $Ar-S-Ar$, $R-S-Ar$
- Class 3. Aliphatic, aromatic, or mixed disulfides (bisthioethers): $R-SS-R$, $Ar-SS-Ar$, $R-SS-Ar$
- Class 4. Heterocyclic compounds of the thiophene type: e.g., dibenzothiophene



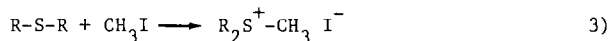
It is generally assumed that any chemical desulfurization process that can remove organic sulfur will do so because of the reactivity of compounds in Class 1, 2, and 3. Heterocyclic compounds in Class 4 are extremely stable to chemical attack and high temperature.

The fundamental approach in this study is based on the different reactivity of methyl iodide toward different organosulfur functions to produce sulfonium compounds. The general scheme of reactions for the various classes of sulfur groups can be summarized as follows (7):

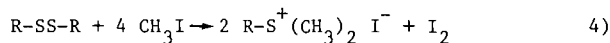
1. Mercaptans:



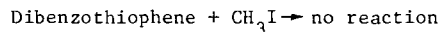
2. Sulfides:



3. Disulfides:



4. Heterocyclic compounds:



The reaction of coal with methyl iodide was used previously (8) to determine the thioether content of coal by measuring the uptake of iodine, presumably associated as iodide with the sulfonium compounds. But the iodine uptake is not a true measure of the thioether content because other compounds, notably heterocyclic nitrogen compounds, can also react resulting in uptake of iodine. To overcome this difficulty, the sulfonium compounds were washed out with a solvent like acetone, and the decrease in the sulfur content was then taken as the indicator of the thioether content (7). A similar procedure was adopted in this work.

Experimental

Materials

The coal used in this study was a high-volatile bituminous coal from the Star mine in Mahaska County, Iowa. The coal was pulverized, screened using U.S. Standard sieves, dried, and analyzed for ash, heating value, and sulfur distribution by ASTM procedures.

Fresh methyl iodide was used directly from the reagent bottle. In some experiments, the reagent was cleaned by shaking with mercury, but no significant difference was noticed in the results.

Methyl Iodide Reaction

A slurry of 20 g coal and 30 ml methyl iodide was placed in a large test tube, covered with foil, and allowed to stand for 3 days at room temperature. The slurry was then filtered and washed with about 2 l. acetone to remove reaction products and unreacted methyl iodide, until the test for iodide (silver nitrate) was negative. The treated coal was dried and analyzed again. Qualitative tests for residual iodide in the treated coal (hydrogen peroxide treatment followed by extraction of iodine into a benzene layer) showed only traces of iodide. The methyl iodide treatments were repeated on enough coal samples to provide a stock of treated coal to be used for the oxydesulfurization experiments.

Oxydesulfurization of Coal in Autoclave

The coal (40 g) was leached for 1 hr with 400 ml solution in a 1-liter autoclave described previously (1). The leaching was done at 150°C under 50 or 200 psia oxygen partial pressure. For non-oxidizing conditions, a partial pressure of 50 psia nitrogen was used. Water or 0.2 M sodium carbonate was used as the leaching solution. The residues from the alkaline leaching step were leached for a second time, also for 1 hr at 150°C, using water, 0.1 M sulfuric acid, 0.1 M phosphoric acid, or 0.2 M sodium carbonate in a nitrogen atmosphere.

Calculations

In order to account for the different levels of ash in the various coal residues, the sulfur content was converted from weight percent to pounds of sulfur per million Btu. This conversion, in effect, allowed the comparison of the organic sulfur content in the organic (i.e., combustible) portion of the coal.

In a few cases, the heating value was not actually determined but was calculated using a formula (1), based on the assumption that the ash-free heating value is relatively constant for the same coal, regardless of the treatment conditions.

Results and Discussion

Removal of Sulfur by the Methyl Iodide Treatment

The results of treating coal with methyl iodide are presented in Table 1. Based on the pounds of sulfur per million Btu, the methyl iodide treatment removed, on the average, 48.3% of the organic sulfur. This seems to indicate that at least one-half of the organic sulfur is in the class that is reactive toward methyl iodide. Since thiophenic compounds are unreactive and disulfide groups react too slowly at room temperature, the reactive portion of the organic sulfur is probably of the sulfide and mercaptan classes.

Further tests were run by treating mineral pyrite with methyl iodide under similar conditions and then washing with acetone. No reaction was observed; the sulfur content was unaffected. Also, simple washing of coal with 2 l. of acetone (without prior methyl iodide treatment) did not alter significantly the ash content, heating value, and sulfur distribution of the coal.

Another possible explanation for the reduction of the organic sulfur may be offered if methyl iodide simply methylates the coal, thus increasing its organic content and decreasing the sulfur content by "dilution." If this observation were a reflection of a methylating effect, then the heating value should have increased, the ash content should have decreased, and the "dilution" should apply to all types of sulfur in coal. Yet the changes in ash content, heating value, and weight recovery were insignificant; and the pyritic and sulfatic sulfur values were fairly constant. It seems, therefore, that organic sulfur was really removed by this procedure. It is not known, however, by what mechanism the sulfonium salts are washed away.

Removal of Sulfur by Oxidative Leaching

The results of leaching the methyl iodide-treated coal are presented in Table 2. The sulfur content should be compared not only to that of the initial coal but also to that of the methyl iodide-treated coal in Table 2. It can be seen that leaching with alkali only, (sample No. 016D), in the absence of oxygen, did not have any effect on the sulfur content. When leaching in the presence of oxygen, the total sulfur content decreased, largely because of a decrease in the inorganic sulfur content. The total sulfur content was lower when higher oxygen partial pressures were used or when the leaching solutions were alkaline. The organic sulfur content was relatively constant, although it appeared slightly higher under non-alkaline conditions when water only was used as the leachant.

In Table 3 results are presented for desulfurization experiments in which a second leaching step was added after the first leaching step with an alkaline solution. The additional leaching was done in a non-oxidizing nitrogen atmosphere, using water, sulfuric acid, phosphoric acid, or sodium carbonate solutions. Aside from one run which appears to be anomalous, the total sulfur content did not seem to be reduced by the second leaching step.

The organic sulfur content, however, appears to be slightly higher than that obtained after one leaching step, under alkaline conditions and in the presence of oxygen. It may be possible that under the nitrogen atmosphere of the second step, some of the pyrite may be converted to elemental sulfur. Such a conversion would be characterized by a decrease in the pyritic sulfur, an increase in the organic sulfur, but no change in the total sulfur. Such a conversion would also be favored by acidic conditions.

Methyl Iodide Treatment of Oxydesulfurized Coal

The results in Table 4 show the effect of methyl iodide treatment on Star coal that had been precleaned by a float-sink technique and subsequently leached for 1 hr with 0.2 M sodium carbonate at 150°C under 50 or 200 psia partial pressure of oxygen. By comparison with the sulfur values in Table 1, the cleaning and leaching apparently removed only the inorganic sulfur, leaving the organic sulfur content largely unaffected. Leaching at higher oxygen partial pressure seemed to remove more total sulfur.

Curiously, subsequent treatment of the leached coal with methyl iodide did not seem to remove any organic sulfur as it did when applied to the raw, unleached coal (see Table 1). This lack of reactivity may be due to physical changes in the coal caused by the high temperature (150°C) of the leaching. Alternatively, the chemical leaching may have caused a conversion of reactive organosulfur groups into unreactive groups. Perhaps also the difference in the particle size (-200 mesh in this set of experiments compared to -150/+200 mesh in previous experiments) can be a contributing factor.

Conclusions

Treatment of coal with methyl iodide followed by extensive washing with a solvent to remove the reaction products has been used to remove approximately one-half of the organic sulfur content in an Iowa high volatile bituminous coal. The pyritic and sulfatic sulfur content was not affected by the methyl iodide treatment. Washing the coal with solvent only did not produce any effect either. On the basis of chemical reactions reported in the literature, it is assumed that the reactive sulfur groups that were removed by this treatment may be organic sulfides or mercaptans.

Subsequent leachings of the methyl iodide-treated coal under various conditions of oxydesulfurization did not reduce further the organic sulfur content. The inorganic sulfur content, however, was reduced by the oxydesulfurization steps. It can be assumed that all the reactive and accessible organic sulfur was removed by the methyl iodide treatment, and further chemical desulfurization was directed only against the inorganic sulfur.

When the coal was first precleaned by a float-sink technique and then leached by the oxydesulfurization procedure, the organic sulfur content was not affected by subsequent treatment with methyl iodide. This lack of reactivity of the organic sulfur toward methyl iodide may be caused by physical or chemical changes in the coal brought about by the high temperature or chemical nature of the oxydesulfurization process.

Acknowledgment

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Table 1. Effect of methyl iodide (MeI) treatment and acetone (Me_2CO) washing on sulfur content of coal.^a

No. ^b	Treatment	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.				S Redn., %	
				Tot.	Pyr.	Sulf.	Org.	Org.	Tot.
001D	None	12579	8.34	2.02	0.98	0.15	0.89	--	--
029D	Me_2CO	12495	8.95	2.06	1.08	0.20	0.78	--	--
003	MeI + Me_2CO	12552	8.29	1.68	1.08	0.17	0.43	50.6	16.8
004	MeI + Me_2CO	12490	8.46	1.62	1.18	0.14	0.30	66.3	19.8
005	MeI + Me_2CO	12506	8.57	1.78	1.04	0.10	0.64	28.1	11.9
Ave (of 003, 004, 005)		12516	8.44	1.70	1.10	0.14	0.46	48.3	15.8

^aStar coal (-150/+200 mesh).

^b"D" denotes average of duplicate analysis.

Table 2. One-step oxydesulfurization of MeI - treated coal.^a

Sample No. ^b	Leach soln.	O_2 psia	Press., psia	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.			
						Tot.	Pyr.	Sulf.	Org.
001D	-- None	--		12579	8.34	2.02	0.98	0.15	0.89
Ave. of 003, 004, 005	-- MeI	--		12516	8.44	1.70	1.10	0.14	0.46
013	H_2O	50		12046	6.75	1.28	0.44	0.17	0.67
006	Na_2CO_3	50		10220	12.90	1.21	0.52	0.16	0.53
014D	H_2O	200		11818	6.68	1.06	0.20	0.12	0.75
012	Na_2CO_3	200		11787	13.02	0.91	0.39	0.08	0.44
016D	Na_2CO_3	0 ^c		12245	7.41	1.63	0.95	0.11	0.57

^aStar coal (-150/+200 mesh), treated with MeI and then leached 1 hr at 150°C with H_2O or 0.2 M Na_2CO_3 under 50 or 200 psia O_2 .

^b"D" denotes average of duplicate analysis.

^cNon-oxidizing atmosphere of 50 psia N_2 partial pressure.

Table 3. Two-step desulfurization of MeI - treated coal.^a

Sample No. ^b	2nd step Leach	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.			
				Tot.	Pyr.	Sulf.	Org.
1st Leach Step with 0.2 <u>M</u> Na ₂ CO ₃ under 50 psia O ₂							
018D	H ₂ O	11119	14.28	1.30	0.67	0.03	0.60
020D	0.1 <u>M</u> H ₂ SO ₄	11529	6.72	1.24	0.46	0.05	0.73
023	0.1 <u>M</u> H ₃ PO ₄	11479	12.26	1.31	0.53	0.03	0.63
024D	0.2 <u>M</u> Na ₂ CO ₃	9042	13.33	1.20	0.52	0.07	0.61
1st Leach Step with 0.2 <u>M</u> Na ₂ CO ₃ under 200 psia O ₂							
027D	H ₂ O	11763 ^c	9.32	0.86	0.21	0.05	0.60
035D	0.1 <u>M</u> H ₂ SO ₄	11614 ^c	6.03	1.03	0.30	0.08	0.65
031D	0.1 <u>M</u> H ₃ PO ₄	11478 ^c	12.27	1.16	0.52	0.05	0.59
033D	0.2 <u>M</u> Na ₂ CO ₃	9831	19.65	1.20	0.65	0.08	0.47

^aStar coal (-150/+200 mesh), treated with MeI and then leached 1 hr at 150°C with 0.2 M Na₂CO₃ under 50 or 200 psia O₂. For 2nd step, leached 1 additional hr at 150°C under 50 psia N₂ with indicated leach solution.

^b"D" denotes average of duplicate analysis

^cH.V. calculated.

Table 4. Methyl iodide (MeI) treatment of leached coal.^a

Sample No. ^b	Treatment	H.V., Btu./lb.	Ash, %	S Content, lb./10 ⁶ Btu.			
				Tot.	Pyr.	Sulf.	Org.
060D	Leached under 50 psia O ₂	9162	9.53	1.29	0.24	0.05	1.00
062D	MeI treatment of Sample 060D	11370	10.63	1.26	0.24	0.01	1.01
064	Leached under 200 psia O ₂	10810	11.71	1.04	0.11	0.02	0.91
065D	MeI treatment of Sample 064	11534	10.56	0.96	0.10	0.01	0.85

^aStar coal (-200 mesh) precleaned and leached 1 hr at 150°C with 0.2 M Na₂CO₃ under 50 or 200 psia O₂.

^b"D" denotes average of duplicate analysis.